KINETIC FRACTIONATION OF LITHIUM ISOTOPES BY DIFFUSION IN WATER

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RESEARCH OBJECTIVES

The mass-dependent fractionation of stable isotopes can occur during a number of physical processes, only some of which are well understood theoretically and well investigated experimentally. In particular, the kinetic fractionation of isotopes during diffusion, though understood for gaseous systems, is not well characterized and understood for condensed systems such as liquid water or silicate melts. In the simple case of diffusion of a monatomic gaseous species in an isothermal gas, the ratio of the diffusivities for two isotopes of an element is proportional to the square root of the inverse ratio of the isotope masses. This arises from the equivalence in kinetic energy for molecules in an isothermal gas. In condensed systems such as silicate melts, this simple relationship does not appear to hold. We undertook experiments in aqueous solutions to better understand the phenomenon of kinetic fractionation during diffusion. Results could provide a signature for diffusion in geochemical systems, as well as add to fundamental understanding of the structure and behavior of ion complexes in aqueous solutions.
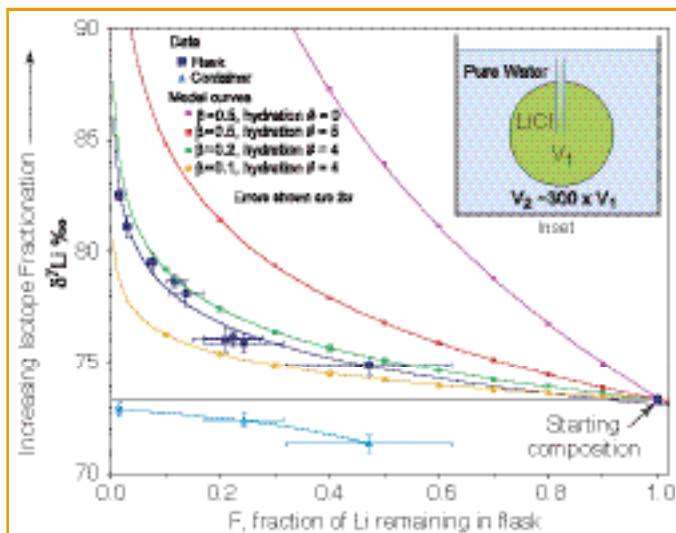

Figure 1. Plot of F, the fraction of Li remaining in the flask, vs. ^{7}Li, a measure of the Li isotopic composition. Large black squares = data for flasks, blue triangles = data for containers. Model curves are shown for different hydration numbers (# of waters in the hydration sphere) and exponential factors (=β). The inset shows the experimental setup, a flask of Li solution immersed and communicating with a larger volume of pure water.

APPROACH

The experimental setup consists of a 0.7 mL glass flask immersed in a larger (~300x) volume container (see inset, Figure 1). The flask is filled with a solution of the element of interest and communicates with the larger container via a thin tube. The experiments reported here used a ~700 ppm lithium chloride (LiCl) solution in the flask and high purity water in the surrounding container. Pairs of flasks and containers were set up and allowed to exchange for periods ranging from 31 days to 99 days. At the end of an experiment, we measured the concentrations of Li remaining in the flask and built up in the container. Lithium isotopic compositions (^{7}Li/^{6}Li ratios) were measured by multiple-collector ICP mass spectrometry (MC-ICPMS).

ACCOMPLISHMENTS

The results of nine experimental runs with durations ranging from 31 to 99 days are displayed in Figure 1, where F, the fraction of the original Li remaining in the bulb, is plotted against δ^{7}Li, a measure of Li isotopic composition. The longest duration experiment left only 1.5% of the original amount of Li in the flask, the balance having diffused into the container volume. As F decreases and Li diffuses from the flask, the isotopic composition of the Li in the flask is fractionated, with more of the heavier ^{7}Li left in the flask than the lighter ^{6}Li. This demonstrates that kinetic fractionation of Li isotopes does occur, in contrast to similar experiments involving magnesium that failed to resolve a fractionation effect.

SIGNIFICANCE OF FINDINGS

Though fractionation was observed, it was not as great as would be predicted by the theory for gaseous diffusion. A portion of the discrepancy may result from Li$^+$ diffusing as a hydrated complex, diluting the ^{6}Li-^{7}Li mass difference. Models and observations suggest that a sphere of four to six water molecules surrounds Li$^+$ ions. But for an exponent of 0.5, as for a gas, it would require a sphere of 11 waters, an improbable number. If the hydration sphere consists of four waters, then an exponential factor of ~0.2 reproduces the data. This may reflect the inelastic nature of interactions between water molecules and the Li$^+$ hydrated complex. Further experiments are being conducted to better understand and independently constrain the exponential factor and the hydration number.

ACKNOWLEDGMENTS